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Note

A Generalization of Fujita's Equation for Sedimentation Equilibrium

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The purpose of this note is to present the formal derivation of a generalized form of Fujita's equation[1] for sedimentation equilibrium on nonideal polydisperse system. His equation is given for the weight-average molecular weight. Yet potentially sedimentation equilibrium can afford to inform us of many other average molecular weights as well. As far as the higher average molecular weights are concerned, application of the method has been practically limited to the pseudoideal system, where the solute-solute interactions apparently vanish. For such systems, there have been published two methods: one is the classical Lansing-Kraemer method,[2] and the other the variable λ method first proposed by Fujita[3] and later extended by Scholte.[4] Although the latter has been proved very useful and reliable, it often becomes infeasible to meet the necessary condition that the system of interest is to be in the pseudoideal state. Therefore, it is highly desirable to develop a new method valid for nonideal systems. An approach relevant to this aim is to extend and generalize Fujita's equation. With such a generalization, we wish to embellish his original work.

We consider a system similar to the one Fujita treated,[1] *i.e.*, an incompressible solution containing a single solvent (component 0) and polymeric solutes of q species (components 1, 2,..., q) differing in molecular weight M but with negligible difference in partial specific volume $\bar{v}$. Then, the basic equation for sedimentation equilibrium reads[1]

$$\lambda M_i c_i = dc_i/d\xi + M_i c_i \sum_{k=1}^{q} B_{ik}(dc_k/d\xi) + \bar{v}\sum_{k=1}^{q} c_k(dc_i/d\xi) + 0(c_i c_k c_m) \qquad (i=1, 2,..., q) \tag{1}$$

where c_i denotes the local equilibrium concentration of solute i in g/ml, B_{ik} stands for the thermodynamic interaction coefficient between solutes i and k, and λ and ξ are, respectively, the generalized speed parameter and the reduced radial distance:

$$\lambda = (1-\bar{v}\rho_o)(b^2-a^2)\omega^2/2RT \tag{2}$$

$$\xi = (r^2-a^2)/(b^2-a^2) \tag{3}$$

Here, a, b, and r are, respectively, the radial distances to the meniscus, to the bottom

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and to a given position of the solution column, ρ_o the solvent density at equilibrium temperature, ω the angular velocity, and RT has got the usual significance. For later convenience, we introduce here further symbols: $c^o=\sum_i c_i^o$ and $c=\sum_i c_i$ designate, respectively, the original and the local equilibrium concentrations, $g_i=c_i^o/c^o$ represents the weight fraction of solute i in the sample, $\theta_i=c_i/c_i^o$ stands for the relative equilibrium distribution of solute i, Δ in ΔX is the operator to take difference in quantity X between the positions a and b.

Now equation 1 can be rewritten in new symbols as

$$\lambda M_i\theta_i g_i=(d\theta_i/d\xi)g_i+c^o M_i\theta_i g_i\sum_k B_{ik}(d\theta_k/d\xi)g_k + c^o\bar{v}\sum_k\theta_k(d\theta_i/d\xi)g_i g_k+0[(c^o)^2] \tag{4}$$

This differential equation suggests that the solution θ_i may be expressed in a polynomial of c^o.[1)]

$$\theta_i(\xi)=\theta_{i0}(\xi)+c^o\theta_{i1}(\xi)+0[(c^o)^2] \tag{5}$$

where the $\theta_{ij}(\xi)$'s are unknown functions of ξ with the restrictions as

$$\int_0^1\theta_{i0}(\xi)\,d\xi=1,\quad \int_0^1\theta_{ij}(\xi)\,d\xi=0,\qquad (i=1,2,\ldots,q;\ j\geqq 1) \tag{6a, b}$$

Combining Eq. 4 with Eq. 5, we obtain a set of differential equations:

$$d\theta_{i0}/d\xi=\lambda M_i\theta_{i0} \tag{7a}$$

$$d\theta_{i1}/d\xi=\lambda M_i\theta_{i1}-\sum_k\{M_i B_{ik}\theta_{ik}(d\theta_{k0}/d\xi)+\bar{v}\theta_{k0}(d\theta_{i0}/d\xi)\}g_k \tag{7b}$$

.....

The first two solutions of $\theta_{ij}(\xi)$'s are as follows:

$$\theta_{i0}=\exp(\lambda M_i\xi)/[\exp(\lambda M_i)-1] \tag{8a}$$

$$\theta_{i1}=\theta_{i0}\sum_k M_i(B_{ik}+\bar{v}/M_k)\left\{\int_0^1\theta_{i0}\theta_{k0}\,d\xi-\theta_{k0}\right\}g_k \tag{8b}$$

with

$$\int_0^1\theta_{i0}\theta_{k0}\,d\xi=\frac{\lambda M_i M_k[\exp\lambda(M_i+M_k)-1]}{(M_i+M_k)[\exp(\lambda M_i)-1][\exp(\lambda M_k)-1]} \tag{9}$$

With these solutions, the following relations may be readily obtained:

$$\Delta(\theta_{i0}\theta_{k0})=\lambda(M_i+M_k)\int_0^1\theta_{i0}\theta_{k0}\,d\xi+0(c^o) \tag{10a}$$

$$\Delta\theta_i=\lambda M_i+\lambda c^o\sum_k M_i[M_i-(M_i+M_k)](B_{ik}+\bar{v}/M_k)\int_0^1\theta_{i0}\theta_{k0}\,d\xi\,g_k+0[(c^o)^2] \tag{10b}$$

Now we differentiate $(s-1)$ times each term of Eq. 4 with respect to ξ, operate Δ to them, and take summation over i to get

$$\lambda^{s+1}\sum_i M_i^{s+1}g_i+\lambda^{s+1}c^o\sum_i\sum_k M_i[M_i^{s+1}-M_i(M_i+M_k)^s](B_{ik}+\bar{v}/M_k)\int_0^1\theta_{i0}\theta_{k0}\,d\xi\,g_i g_k$$
$$=\Delta(d^s c/d\xi^s)/c^o+\lambda^{s+1}c^o\sum_i\sum_k M_i M_k(M_i+M_k)^s(B_{ik}+\bar{v}/M_k)\int_0^1\theta_{i0}\theta_{k0}\,d\xi\,g_i g_k + \text{higher terms in } c^o \tag{11}$$

Following the Lansing-Kraemer expressions[2)] for average molecular weights and their apparent ones,

$$M_w M_z \cdots M_{z+s-1} = \sum M_i^{s+1} g_i \tag{12b}$$

$$(M_w M_z \cdots M_{z+s-1})^{app} = \Delta(d^s c/d\xi^s)/(\lambda^{s+1} c^o) \tag{12a}$$

we may reduce the above equation into the form below:

$$(M_w M_z \cdots M_{z+s-1})^{app} = M_w M_z \cdots M_{z+s-1} + c^o \sum_i \sum_k M_i [M_i^{s+1} - (M_i + M_k)^{s+1}] \times (B_{ik} + \bar{v}/M_k) \int_0^1 \theta_{i0} \theta_{k0} d\xi \, g_i g_k + \text{higher terms in } c^o \tag{13a}$$

or after reciprocating and re-expanding in the form of

$$1/(M_w M_z \cdots M_{z+s-1})^{app} = 1/M_w M_z \cdots M_{z+s-1} + c^o (M_w M_z \cdots M_{z+s-1})^{-2} \times \sum_i \sum_k M_i [(M_i + M_k)^{s+1} - M_i^{s+1}] (B_{ik} + \bar{v}/M_k) \int_0^1 \theta_{i0} \theta_{k0} d\xi \, g_i g_k + \text{higher terms in } c^o \tag{13b}$$

This is the generalized equation we aimed to derive, and Fujita's equation is seen to be a special case of Eq. 13b. With $s=0$, the equation can be written as

$$1/(M_w)^{app} = 1/M_w + c^o (M_w)^{-2} \sum_i \sum_k M_i M_k (B_{ik} + \bar{v}/M_k) \int_0^1 \theta_{i0} \theta_{k0} d\xi \, g_i g_k + \text{higher terms in } c^o \tag{14}$$

where

$$(M_w)^{app} = \Delta c/(\lambda c^o) \tag{15}$$

The form of Eq. 13b suggests that the higher average molecular weights are formally obtained by successive extrapolations. As is well-known, the number-average molecular weight is also determined by sedimentation equilibrium, but equation 13b doesn't include this case. It is because an additional experimental condition must be satisfied for this purpose. So we will discuss it in a separate paper.

On applying Eq. 13b to analyses of experimental results, one must pay close attention to the λ-dependence of the function, $\int_0^1 \theta_{i0} \theta_{k0} d\xi$. In regard to this problem, one may refer, for examples, to the papers.[5] Experimentally only the curves of $c(r)$ and $dc(r)/dr$ are observable with the optical devices installed in an ultracentifuge, no derivatives higher than the second being directly obtained. However, advances in computer techniques is promising to enable us to synthesize the curve of $c(r)$ or $dc(r)/dr$ from experimental results and to evaluate its derivatives successively with accuracy.[5]

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